Communications.

STUDIES IN THE CHEMISTRY OF TARTARIC ACID.

BY THE LATE B. J. GROSJEAN.

[Mr. B. J. Grosjean was for many years the chemist at Sir J. B. Lawes's Tartaric and Citric Acid Factory, Millwall. The following abstract of some of his unpublished investigations has been compiled by Mr. R. Warington from reports made by Mr. Grosjean, and from his Laboratory Note-books. The results are made public by Sir J. B. Lawes's kind permission. Further investigations by Mr. Grosjean will be found in the *Journal of the Chemical Society* for July in the present year.]

I. ACTION OF SOLUTIONS OF POTASSIUM AND SODIUM SULPHATE ON CALCIUM TARTRATE.

The observations recorded in this section were commenced in 1876, and continued at intervals in the two following years.

Although a solution of calcium sulphate produces no precipitate in solutions of neutral tartrates, yet an excess of moist gypsum will, as is well known, precipitate almost the whole of the tartaric acid from neutral solutions of potassium tartrate. This reaction is, in fact, regularly employed in the manufacture of tartaric acid. The crude tartar in the factory is first boiled with water and neutralised with chalk (whiting). Half the tartaric acid is thus precipitated as calcium tartrate, while the other half remains in solution as neutral tartrate of potassium. The addition of an excess of moist gypsum decomposes this potassium tartrate, sulphate of potassium and calcium tartrate being produced. Mr. Grosjean has found that under certain conditions the reaction last mentioned may be entirely reversed, and that by attacking calcium tartrate with a hot and sufficiently strong solution of potassium or sodium sulphate, practically the whole of the tartaric acid may be brought into solution as tartrate of potassium or sodium. The results obtained with solution of potassium sulphate shall be first mentioned.

1. 4grms. of calcium tartrate were heated with 30c.c. of water, 10grms. of potassium sulphate next added, and the whole heated in a water-bath for half an hour. The contents of the beaker were then placed on a vacuum filter, and the residue quickly washed with water. The small quantity of lime in the filtrate and washings was removed with a little potassium oxalate, the liquid concentrated to 60c.c., and the tartaric acid present precipitated as acid potassium tartrate by the addition of 2grms. of citric acid and 3grms. of potassium chloride. The tartaric acid obtained amounted to 2·1931grms. The calcium tartrate taken (analysed by digestion with potassium oxalate and precipitation with citric acid) had contained 2·2033grms. of tartaric acid. The action of the potassium sulphate was thus very complete, 99·5 per cent. of the tartaric acid taken being obtained as potassium tartrate.

2. A duplicate experiment was made, the only alteration being that after heating the whole was allowed to stand an hour and become cold before filtering commenced. This alteration did not distinctly affect the result, the tartaric acid found in solution being 2·1627grms., or 98·2 per cent. of that taken as calcium tartrate.

Two series of experiments were next made to ascertain the effect of varying proportions of potassium sulphate, and also the influence of varying degrees of dilution. The mode of conducting the experiments was in general that above described. The calcium tartrate employed was not quite pure; the tartaric acid it contained was determined by the neutralising power of its ash. The amount of water present during each digestion was also somewhat roughly ascertained. The results of the experiments nevertheless plainly indicate the general influence which different proportions of potassium sulphate and of water exert in this reaction. The results will be found in Table I.

TABLE I.—TARTARIC ACID OBTAINED AS POTASSIUM TARTRATE BY THE ACTION OF POTASSIUM SULPHATE ON CALCIUM TARTRATE.

No.	Materials Taken—Grams.			Tartaric Acid obtained as Potassium Tartrate.		
	Tartaric Acid as Calcium Tartrate.	Potassium Sulphate.	Water.	In Grams.	For 100 taken.	For 100 of Potassium Sulphate.
1.	2·2033	10	30	2·1931	99·5	21·9
2.	..	..	..	2·1627	98·2	21·6
a	1·1270	5	15	1·0690	94·9	21·4
b	..	..	25	1·0035	89·0	20·1
c	..	..	50	0·9178	81·4	19·0
d	..	..	100	0·7332	65·1	14·7
e	0·5635	2·5	15	0·4650	83·4	18·6
f	..	2·0	..	0·3557	63·1	17·8
g	..	1·0	..	0·0060	1·1	0·6

In experiments *a*—*d* the quantities of calcium tartrate (2grms.) and of potassium sulphate (5grms.) remain constant, while the quantity of water is varied. The results plainly show that as the proportion of water increases, the decomposing effect of the potassium sulphate diminishes.

In experiments *e*—*g* the proportion of potassium sulphate is varied, the other bodies remaining constant. We here see the prejudicial influence of dilution intensified by a gradual reduction in the proportion of the potassium sulphate. According to the last experiment, 1grm. of potassium sulphate with 15c.c. of water has scarcely any decomposing effect when heated with 1grm. of calcium tartrate.

Mr. Grosjean soon ascertained that the product of the action of potassium sulphate on calcium tartrate was not calcium sulphate, but the double sulphate of calcium and potassium. He found also that the latter salt was readily decomposed by water. Ditte (*Compt. Rend.* 79, 1254; *Jour. Chem. Soc.* 1875, 332) has shown that the double sulphate can exist in contact with water only when a certain excess of potassium sulphate is present in solution. At 15° the solution must contain at least 2·5 per cent. of potassium sulphate for the double salt to remain permanent; if less is present, the double salt is decomposed by the water till sufficient potassium sulphate is brought into solution to produce the condition of equilibrium mentioned. The higher the temperature the greater will be the excess of potassium sulphate required to produce equilibrium. Mr. Grosjean studied the action of water on the double sulphate of calcium and potassium at a temperature of about 20°. Three successive treatments with water gave solutions containing respectively 2·96, 2·86, 2·81 per cent. of potassium sulphate. These results agree with the earlier ones of Ditte, with which Mr. Grosjean was, I believe, at this time unacquainted. The same three solutions contained respectively 0·19, 0·17, 0·17 per cent. of calcium sulphate.

The facts just mentioned seem to throw some light on the results of the previous experiments. If we look at the reaction between potassium sulphate and calcium tartrate in its simplest aspect, and shut out from view any mere influence of mass, we shall probably conclude that calcium tartrate containing

1grm. tartaric acid would require for its decomposition the amount of potassium sulphate (2·323grms.) necessary to produce sulphate of calcium and potassium, with, in addition, an excess of potassium sulphate amounting to 2·5 per cent. of the solution at 15°, and increasing with a rise in the temperature employed. With each increase in the dilution there would clearly be an increase in the quantity of potassium sulphate required to produce the excess demanded. Mr. Grosjean does not appear to have made any trials as to the possibility of the reaction taking place at a low temperatures. All his experiments were conducted near a boiling heat.

The reaction with sodium sulphate differs in several respects from that with potassium sulphate. The precipitate produced by the action on the calcium tartrate is not nearly so bulky. To what extent it consists of a double sulphate of calcium and sodium was not determined. At a temperature near boiling, and with a favourable proportion of water, a considerably smaller quantity of sodium sulphate than of potassium sulphate is required to decompose an unit of calcium tartrate. On cooling, however, a reverse action sets in, and a considerable part of the tartaric acid again becomes tartrate of calcium. In the case of potassium sulphate we have already seen that the action is not reversed on cooling.

The experiments quoted in the following table are best comparable with those numbered *a*—*g* in the trials with potassium sulphate. The reaction was in all cases conducted on a water-bath, and the contents of the beaker transferred while hot to a vacuum filter. The tartaric acid dissolved was determined by the ignition method.

TABLE II.—TARTARIC ACID OBTAINED AS SODIUM TARTRATE BY THE ACTION OF SODIUM SULPHATE ON CALCIUM TARTRATE.

No.	Materials Taken—Grams.			Tartaric Acid obtained as Sodium Tartrate.		
	Tartaric Acid as Calcium Tartrate.	Sodium Sulphate.	Water.	Grams.	For 100 taken.	For 100 of Sodium Sulphate.
1	2·2212	6·00	15	1·0830	48·7	18·1
2	1·6629	6·00	30	1·6125	98·8	27·1
3	1·1106	3·00	..	0·9211	83·0	30·7
4	..	1·50	..	0·1551	14·0	30·3
5	..	0·75	..	0·2168	19·5	28·9

It appears from these experiments that sodium sulphate may be used economically as a 10 per cent. solution. At this strength 3grms. of sodium sulphate are almost as efficient as 5grms. of potassium sulphate, as may be seen by comparing experiments *c* in Table I. with experiment 3 in Table II. In experiment 1 the inferior result per unit of sodium sulphate seems due to the employment of too small a proportion of water. When the sodium sulphate does not exceed 10 per cent. of the solution, very considerable variations, both in the degree of dilution, and the proportion of calcium tartrate present, may apparently occur without producing any large alteration in the decomposing efficiency of the unit of sodium sulphate: a result certainly different from that observed in the experiments with potassium sulphate.

It is clear that further experiments are required to elucidate the subject.* If, however, we may assume that a double sulphate of sodium and calcium was not formed in experiments 2-5, many of the differences from the results obtained with potassium sulphate admit of at least a partial explanation. On this hypothesis the sodium sulphate would not be partially precipitated with the calcium sulphate, and a much smaller proportion of sodium sulphate than of potassium sulphate would therefore be required to decompose an unit of calcium tartrate. Dilution would also have a far less injurious effect on the sodium reaction, for here it is not necessary, as in the potassium reaction, to maintain a certain percentage of alkali sulphate in the solution in order to determine the reaction with the calcium tartrate. But this advantage on the side of the sodium sulphate is confined to a high temperature, for, on cooling, the calcium sulphate again combines with the tartaric acid. Not so in the potassium reaction. Here there is no calcium sulphate, and the double sulphate of calcium and potassium that is present becomes, as we have seen, more stable as the solution cools.

If any of the solutions of potassium or sodium tartrate obtained in the above experiments are considerably diluted, and an excess of solid sulphate of calcium added, nearly the whole of the tartaric acid will be precipitated as calcium tartrate.

II. DESTRUCTION OF CITRATES AND TARTRATES BY HYDROGEN PEROXIDE.

The following experiment, made in 1880, will serve as an example of the results obtained:—

5c.c. of a saturated solution of tripotassic citrate were treated with 20c.c. of dilute sulphuric acid and 40c.c. of a solution of hydrogen peroxide (1 vol. = 10 vols. oxygen). The whole was then boiled in a glycerine bath for two hours. At the end of this time the solution had become neutral. The acid destroyed was equivalent to about 1grm. of citric acid. When the action was pushed further by new additions of hydrogen peroxide the solution became alkaline. In a blank experiment, omitting the hydrogen peroxide, no loss of acidity was observed. On boiling a solution of potassium bitartrate, or an acidified solution of Rochelle salt, with hydrogen peroxide, the solutions became alkaline. The hydrogen peroxide has apparently no action in the cold, at least not in a short time.

III. DESTRUCTION OF NEUTRAL TARTRATES WHEN THEIR SOLUTIONS ARE HEATED WITH AN IRON SALT.

The following experiments were made in 1880:—

1. A mixture containing 2grms. tartaric acid and 0·3grm. of ferrous sulphate, in 200c.c. of water, was neutralised with potash, and then concentrated to 50c.c. The tartaric acid was precipitated by the addition of 2·5grms. of citric acid with 5grms. of potassium chloride, and continuous stirring for ten minutes. The potassium bitartrate obtained was equal to only 91·0 per cent. of the tartaric acid taken.

2. The first-named experiment was repeated, but the neutralisation with potash was omitted. The concentrated solution was precipitated with 2c.c. of a saturated solution of potassium citrate, 0·5grm. of citric acid and 5grms. of potassium chloride being also added. The tartaric acid found was 99·6 per cent. of that taken.

Many similar experiments appeared to show that little, if any, loss of tartaric acid occurred during the evaporation of solutions containing iron when these solutions contained free tartaric acid and not tartrates. The subject clearly, however, requires further experiments. The power of ferric salts to decompose tartaric and other organic acids under the influence of light has been noticed by many chemists.

IV. DETERMINATION OF FREE SULPHURIC ACID IN TARTARIC ACID LIQUORS.

The experiments detailed in this section were made in the years 1880 and 1881. They relate both to the qualitative and quantitative determination of sulphuric acid in tartaric liquors.

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* Fritzsche (*J. Pr. Chem.*, 72, 291) obtained the double sulphate of sodium and calcium only in very strong solutions.

In a tartaric acid factory it is necessary to have some simple means of ascertaining when an excess of sulphuric acid has been added for the decomposition of calcium tartrate. The test employed by the workmen consists in adding to a portion of the liquor a few drops of solution of calcium chloride. If in a few minutes a precipitate of gypsum appears, it is known that an excess of sulphuric acid is present. This test is certainly ingenious. Barium chloride would here be quite unsuitable, as the liquor is saturated with sulphate of calcium. Mr. Grosjean made a study of this factory test. He found that under suitable conditions it was capable of detecting a very small quantity of sulphuric acid, and that by its use under known conditions a rough estimate may often be formed of the quantity of acid present.

A selection of the experiments made will be found in the following table. All experiments were made with 50c.c. of a 10 per cent. solution of tartaric acid, to which known quantities of sulphuric acid had been added. The tartaric solution was saturated with gypsum at 35°, to imitate the conditions usual in the factory during the decomposition of calcium tartrate; the solution was cooled to 15° before treatment; the calcium chloride was employed as a saturated solution. The amount of free sulphuric acid in each solution is expressed in terms of brown oil of vitriol, and also in its equivalent of sulphuric anhydride. The former expression is employed as the one most suitable to the manufacturer, brown oil of vitriol (sp. gr. 1,713) being the acid he employs.

TABLE III.—RESULTS OF ADDING SATURATED CALCIUM CHLORIDE SOLUTION TO 50C.C. OF A 10 PER CENT. SOLUTION OF TARTARIC ACID CONTAINING KNOWN QUANTITIES OF SULPHURIC ACID.

Sulphuric Acid Present. Per Cent.		Calcium Chloride Solution taken.	Time required to produce Turbidity.
Reckoned as B. O. V.	Reckoned as Sulphuric Anhydride.		
0·5	0·315	15 drops	Not in 2 hours
0·8	0·501	"	30 minutes
1·2	0·756	"	15 "
1·2	..	30 drops	8 "
1·2	..	15 drops	Turbid at once
0·8	0·501	"	8 minutes
0·8	..	60 drops	5 "
0·8	..	90 drops	4 "
0·8	..	120 drops	3 "
0·8	..	10 c.c.	2 "
0·8	..	21 c.c.	Turbid at once
0·4	0·252	31 c.c.	"
0·5	0·315	7 c.c.	5 minutes
0·2	0·126	18 c.c.*	5 "
0·1	0·063	25 c.c.	5 "

These results show that when the proportion of sulphuric acid present is very small, very large amounts of calcium chloride are required to give rise to a precipitate of gypsum. Both the delicacy and rapidity of the reaction are increased in proportion to the amount of calcium chloride employed. By constructing a table somewhat similar to the above, it becomes possible, when testing new factory liquors, containing nearly the same proportion of tartaric acid and saturated with gypsum, to ascertain approximately the percentage of free sulphuric acid present by observing the proportion of calcium chloride required to produce a turbidity in five minutes.

Mr. Grosjean found that a saturated solution of gypsum, containing neither sulphuric nor tartaric acid, yielded a precipitate on the addition of a considerable quantity of calcium chloride. It is clear, however, that gypsum alone will not produce a precipitate in the presence of much tartaric acid. A few experiments were made on the effect of varying proportions of tartaric acid. In solutions containing 1 per cent. B.O.V. an increase in the tartaric acid from 5 to 10 per cent. appears to retard the precipitation by calcium chloride.

The quantitative method already suggested for the determination of sulphuric acid in tartaric liquors (*Jour. Chem. Soc.*, 1875, 981) consisted in first pouring the liquor into alcohol to precipitate sulphates, and then precipitating the sulphuric acid in the alcoholic solution by the addition of calcium chloride. As the calcium sulphate thus obtained is apt to contain calcium tartrate, it was recommended that this precipitate should finally be dissolved in hydrochloric acid, and the sulphuric acid thrown down with barium chloride. Mr. Grosjean found, by a test experiment with a known quantity of sulphuric acid, that the whole of the sulphuric acid is not finally precipitated by barium chloride when the calcium precipitate is much contaminated by tartrate. He found it more accurate to ignite the mixed sulphate and tartrate of calcium, treat the ash with strong nitric acid to oxidise any sulphide, and then, after driving off the excess of acid by heat, to add alcohol, and collect and weigh the calcium sulphate.

V. DETERMINATION OF TARTARIC ACID BY PRECIPITATION AS POTASSIUM BITARTRATE.

The method formerly proposed for determining the tartaric acid in the tartaric acid liquors of a factory (*Jour. Chem. Soc.*, 1875, 976) consists in precipitating the tartaric acid with an excess of tripotassic citrate, collecting and washing the potassium bitartrate produced, and determining its amount by titration with standard alkali. Mr. Grosjean's observation that the precipitation of the bitartrate was complete after ten minutes' continuous stirring at 10° to 15° has greatly facilitated the use of this method. The washing of the precipitate was at first performed with alcohol, or with a cold saturated solution of potassium bitartrate; but for these washing fluids a 5 per cent. solution of potassium chloride, saturated with potassium bitartrate, was soon substituted. Mr. Grosjean found (*Trans. Chem. Soc.*, 1879, 348) that this solution contained at 12° but one part of potassium bitartrate in 3·213 of solution.

A cognate method to the above was proposed at the same time (*Jour. Chem. Soc.*, 1875, 972) for the determination of tartaric acid in lees. In this case the whole of the tartaric acid is brought into the condition of neutral potassium tartrate by acting on the lees with potassium oxalate and neutralisation with potash, and the tartaric acid is then thrown down as potassium bitartrate by the addition of citric acid.

Both these methods Mr. Grosjean patiently and thoroughly examined. His results relative to the great latter form of the method have been already in part communicated to the Chemical Society (*Trans.* 1879, 341). His experiments on the application of the method to the analysis of tartaric acid liquors have now to be described. The investigation was chiefly conducted during the years 1880 and 1881.

The conclusion finally arrived at by Mr. Grosjean was that the method was liable to two errors in opposite directions. (1) An error of excess, due to the precipitation of an acid citrate of potassium with the potassium bitartrate; (2) an error of deficiency, due to the solubility of potassium bitartrate in solutions of citric acid and citrate of potassium. He believed that perfectly correct results were only obtained when these errors balanced each other.

Mr. A. H. Allen had early called attention (*Chem.*

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* This quantity is approximate only.

News, 1875, 31, 278) to the precipitation of an acid potassium citrate from a solution containing citric acid and potassium acetate in proof spirit; but as no alcohol was present in our solutions, and the precipitate produced in the reaction quoted is freely soluble in the washing fluid (5 per cent. potassium chloride saturated with bitartrate) we employed, neither Mr. Grosjean nor I at first considered that the presence of an acid citrate in the washed bitartrate was at all probable. The following facts subsequently led Mr. Grosjean to a different conclusion:—

1. In trials with known quantities of tartaric acid, the acidity of the bitartrate obtained would be deficient unless a rather considerable excess of citric acid was present at the time of its precipitation (*Trans. Chem. Soc.*, 1879, 348). When the excess of citric acid was too small, and the result deficient, no further amount of bitartrate was precipitated on adding citric acid to the filtrate.

2. In test experiments with known quantities of tartaric acid the potassium bitartrate precipitated by certain proportions of potassium citrate would have an acidity equivalent to more than the tartaric acid taken. When tartaric acid was used alone the excess would seldom exceed 1 per cent., but when much free sulphuric acid was originally present the excess might reach 3 to 4 per cent., unless extreme pains were taken in washing the precipitate.

3. Great difficulty was frequently experienced in washing the bitartrate precipitate so that the acidity of the drain water should be no greater than the acidity of the washing fluid. The first stages of the washing would be easily accomplished, but when the washing seemed nearly completed the acidity of the drain water would often obstinately remain a little above that of the washing fluid, notwithstanding a very large amount of washing. The most effective mode of washing was to stir the precipitate with the washing fluid in a beaker, and repeat this treatment several times before transferring the precipitate to the filter.

4. Precipitates of bitartrate redissolved in a small volume of hot water and thrown down again by cooling, with the addition of potassium chloride, would frequently lose 2 per cent. or more of their acidity. Bitartrate thus reprecipitated always washed with great ease.

5. Citric acid could be detected in the washed precipitates. The mother liquid obtained in reprecipitating the bitartrate (see preceding paragraph) was neutralised with soda and treated with calcium chloride. After long standing in the cold, to separate a little calcium tartrate, the clear solution was boiled and a small quantity of calcium citrate obtained.* A little citrate was equally detected in the washed bitartrate obtained in the analysis of lees by the oxalate method.

The above facts all point to an error of excess, due to the precipitation of a small quantity of an acid citrate. The liability to an opposite error from the solubility of bitartrate in citric acid, and especially in citrate of potassium, is evident from the results already published (*Jour. Chem. Soc.*, 1875, 946) relating to the solubility of potassium bitartrate in various acids and salts. Here, again, the source of error will be greater when the original solution contains sulphuric acid, the quantity of citric acid produced in the reaction being thus increased, and also the difficulty of avoiding an undue excess of potassium citrate.

In Tables IV. and V. will be found a few series of test experiments, in which the same tartaric solution was treated with varying proportions of potassium citrate. The tartaric solutions taken purposely contained (save in Series IV.) a very large proportion of sulphuric acid, thus resembling the worst liquors of a factory. In all these experiments the amount of tartaric acid found (shown by the acidity of the washed precipitate) rises with increasing additions of potassium citrate till a maximum yield is obtained. Beyond this point each further addition of potassium citrate occasions a diminution in the tartaric acid obtained.

TABLE IV.—DETERMINATIONS OF TARTARIC ACID IN TARTARIC LIQUORS, VARYING PROPORTIONS OF POTASSIUM CITRATE BEING EMPLOYED.

Series I.		Series II.		Series III.	
grms. Tartaric Acid...... 2 Sul. Acid (B.O.V.).. 3		grms. Tartaric Acid .... 2 Sul. Acid (B.O.V.) 4		grms. Tartaric Acid ...... 2·0 Sulph. Acid (B.O.V.) 4·0 Phosphoric Anhydride 1·0 Potassium Alum.... 2·0 Ferrous Sulphate .. 0·3	
Potassium Citrate taken.	Product per 100 of Tartaric Acid.	Potassium Citrate taken.	Product per 100 of Tartaric Acid.	Potassium Citrate taken	Product per 100 of Tartaric Acid.
c.c.		c.c.		c.c.	
12	99·0	13	97·6	14	96·5
13	101·3	14	101·1	15	96·7
14	97·8	16	97·6	16	97·9
16	96·2	18	96·2	17	99·6
17	91·4	23	93·1	18	100·6
18	91·1			20	98·7
				23	95·1

In each of the experiments in Series I. and II. the quantities of tartaric and sulphuric acid named in the table, with 5grms. of potassium chloride, were dissolved in such a volume of water that the addition of the potassium citrate mentioned in the table would bring the whole to 50c.c. The ingredients being mixed, the whole was stirred for ten minutes, the temperature being kept between 10° and 15°. The precipitated bitartrate was naturally mixed with much potassium sulphate. It was washed with a 5 per cent. solution of potassium chloride, saturated with bitartrate. The commencement of the washing was by decantation, 25c.c. of the washing fluid being successively employed. The washing was continued on a vacuum filter, and was maintained till the acidity of the drain-water was permanently only very slightly above the acidity of the washing fluid: to accomplish this half a litre of the washing fluid was generally required.

The experiments in Series III. were made at an earlier date than the preceding. The ingredients taken represent a very bad old liquor. The volume of the solution was in all cases 45c.c.: to this the potassium citrate named in the table was added, with 5grms. of potassium chloride, and the whole stirred for ten minutes at 15°. The washing was conducted on a vacuum filter, 200c.c. of washing fluid being employed.

In Series IV. and V., Table V., the precipitation and washing were conducted exactly as in I. and II. The precipitates were then redissolved in 50c.c. of hot water, 5grms. of potassium chloride added, and the whole quickly cooled with stirring to 15°, at which temperature stirring was continued for ten minutes. From this purified precipitate all adhering acidity was readily removed by the ordinary washing fluid. The maximum product obtained in these purified precipitates is seen to be 97·5 to 97·9 per cent. of the tartaric acid taken. The unavoidable loss attending reprecipitation from 50cc. of a 10 per cent. potassium chloride solution would, however, be nearly 0·5 per cent., and this may fairly be added to the above figures.

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* Mr. Grosjean found that a good method of testing a calcium salt for tartaric acid was to dissolve in a small quantity of acetic acid, and add a considerable amount of potassium chloride. Potassium bitartrate is then precipitated if tartaric acid is present.

TABLE V.—DETERMINATIONS OF TARTARIC ACID IN TARTARIC LIQUORS, WITH VARYING QUANTITIES OF POTASSIUM CITRATE; THE WASHED PRECIPITATES REDISSOLVED AND REPRECIPITATED.

Series IV.		Series V.	
Tartaric Acid—2 grams.		Tartaric Acid—2 grams. Sul. Acid (B. O. V.)—2 grams.	
Potassium Citrate taken.	Product per 100 of Tartaric Acid.	Potassium Citrate taken.	Product per 100 of Tartaric Acid.
c.c.		c.c.	
2·0	97·4	8	95·5
2·5	97·9	10	96·2
3·0	97·1	11	97·5
..	..	12	91·1

The final conclusion arrived at by Mr. Grosjean was that in all accurate determinations of tartaric acid in factory liquors it was necessary to make a preliminary series of experiments with graduated quantities of potassium citrate, with the view of discovering the proportion of citrate which gave the precipitate of maximum acidity. This series of experiments need not take long, as stirring for ten minutes suffices to precipitate the bitartrate, and for the present purpose a moderate amount of washing would suffice. The right proportion of citrate being ascertained, a final determination would be made with this quantity, the precipitate in this last experiment being very thoroughly washed after the method employed in the experiments of Series I. and II. The acidity of the bitartrate thus obtained would correctly show the tartaric acid present if the original liquor contained but little sulphuric acid, or would be about 1 per cent. in excess of the truth if much sulphuric acid was present.*

In Mr. Grosjean's already published paper (*Trans. Chem. Soc.*, 1879, 352), he states that he is in the habit of removing excess of sulphuric acid from a tartaric liquor by neutralisation with potash, and allowing the potassium sulphate to crystallise out before proceeding to the precipitation of the tartaric acid, which is then effected by citric acid. This method was afterwards abandoned. In impure liquors the potash produced a gelatinous precipitate difficult to wash. Experience also showed that a neutralised tartaric liquor containing iron suffered loss of tartaric acid during concentration. (See Section III. of this paper). The precipitation of the impure tartaric liquor with excess of whiting, and the decomposition of the precipitate with potassium oxalate, recommended by him in the same paper (*ibid.*, 352), were also given up, test experiments showing low results, the cause of which was, however, not fully traced out. In the case of very bad old liquors it is possible that potassium alum may be precipitated on adding the potassium citrate. This precipitation of alum is due, Mr. Grosjean showed, to its small solubility in a solution containing potassium sulphate, a salt which is formed in abundance on added potassium citrate to a liquor rich in sulphuric acid. When alum has been precipitated along with the potassium bitartrate the result of the analysis will show a deficiency, if the washing is conducted with the usual 5 per cent. solution of potassium chloride saturated with bitartrate. The alum readily dissolves in this fluid, and forms a solution in which potassium bitartrate is readily soluble. Mr. Grosjean confirms the former observation (*Jour. Chem. Soc.*, 1875, 979) that the presence of phosphoric acid in sufficient quantity effectually prevents the precipitation of alum. When, however, both phosphoric acid and alumina are present, it is necessary to collect the precipitated bitartrate immediately after the ten minutes' stirring, as a gelatinous precipitate of aluminium phosphate is apt eventually to occur.

VI. DETECTION OF TARTARIC ACID IN CITRIC ACID.

Cailletet's method (*Jour. Chem. Soc.*, 1879, abstracts 674) answers well. 3grms. of citric acid, with 0·03 grm. of tartaric acid (1 per cent.), were dissolved in 65c.c. of water, 0·2grm. of sulphuric acid and 10c.c. of a saturate solution of potassium bichromate added. In 20 minutes the solution was quite dark in colour, while a comparative solution containing citric acid only remained for several hours light-coloured. Next day the purely citric solution was dark, but still transparent, while that containing 1 per cent. of tartaric acid had become opaque.

VII. DETERMINATION OF ORGANIC ACIDS FROM THE NEUTRALISING CAPACITY OF THE ASH OF THEIR SALTS.

This simple mode of determination is frequently adopted in the analysis of tartrates and citrates. Mr. Grosjean was convinced that potassium and sodium salts must always be ignited at a low temperature, that of an ordinary spirit-lamp flame, if loss of base is to be avoided. With calcium salts no such precaution was needed.

VIII. STANDARDISING OF ALKALI USED FOR TITRATION.

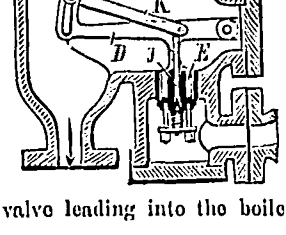
The best material for standardising alkali is pure bitartrate of potassium. It is easily prepared, may be dried without alteration at 100°, is not hygroscopic, and being of low acidity a large weight may be taken for a determination. Delicate litmus paper answers best to ascertain the point of neutralisation. If the bitartrate is prepared from commercial cream of tartar it must be first recrystallised from a hydrochloric solution to remove calcium tartrate, and again crystallised from water; but the simplest method is to start with pure tartaric acid and potassium carbonate.

Journal and Patent Literature.

I.—GENERAL PLANT, APPARATUS, AND MACHINERY.

Improvement in Feed Regulators for Steam Boilers. A. Monski, Eilenburg. Ger. Pat. 22500, October, 1882.

The improvement applies to apparatus, provided with



a water-inlet valve leading into the boiler, and being

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* It is clearly very desirable to have some means of knowing, at least approximately, when a sufficient amount of potassium citrate has been employed. When the amount of tartaric acid present is partly known, it is useful to remember that 1grm. of tartaric acid may be precipitated by about 1cc. of a saturated solution of potassium citrate. When much free sulphuric acid is present, potassium sulphate is first precipitated as a fine powder. The commencement of the precipitation of bitartrate may generally be recognised by the formation of streaks on the side of the vessel when rubbed by the stirrer. When this point is reached a measured quantity of potassium citrate solution proper for the tartaric acid presumed to be present can then be added. It is obvious, also, that the citrate may be added till a drop of the clear liquid removed to a watch-glass gives no more precipitate when treated with a very small quantity of fresh citrate, and the mixture rubbed with a glass rod.—R. W,